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Page 7

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PRELIMINARY PROGRAM
ACS spring meeting, Las Vegas Page 28
Surfactants face slow,
steady growth Page 13

Cover: Photo by Fred Maroon

2	Letters
3	Editor's Page
	Concentrates
12	Business
20	Government
21	Science/Technology

	The Departments
38	ACS News
38	People
50	Newscrips

News of the Week

- **Contract negotiations** between oil refinery members of OCAW and oil companies are under way but the parties are far apart on wages and other benefits. **Page 4**
- **Chemical trade and scientific exchanges** will be affected little by President's sanctions against the U.S.S.R. **Page 4**
- **Former NIH director Donald Fredrickson** speaks out on NIH's efforts to cope with the recombinant DNA controversy. **Page 5**
- **Arkansas law** mandating balanced treatment for creationism and evolution struck down in federal court. **Page 5**
- **Occupational safety and health movement** predicted to become quieter with less emphasis on regulation. **Page 6**
- **R&D budgets for fiscal 1982** are shrinking in terms of real dollars in all areas but defense. **Page 6**

News Focus

- **97th Congress' second session** likely will be dominated by economic issues and Administration may find stronger resistance to its programs as Democrats and Republicans alike face an election year. **Page 7**

Business

- **Surfactants market is big and mature**—7 billion lb in 1980 and growing about 2% per year—but the industry could be in for some surprises. **Page 13**

International

- **New textile trade protocol** has been agreed to at GATT's Geneva headquarters; concern remains among EEC countries about effects of imports. **Page 19**

Technology

- **Microencapsulation technique** for producing monoclonal antibodies developed by Damon Biotech is less expensive, simplifies isolation and purification, and doesn't require the use of laboratory animals. **Page 22**
- **Pressurized filter** provides for continuous cleaning action enabling clarification of process liquids with solid contents as high as 2000 ppm. **Page 23**

Books

- **"Cosmic Dawn—The Origins of Matter and Life"** by Eric Chaisson paints a big picture of cosmic evolution and ends on an optimistic note for the future. **Page 24**
- **Prudent handling of hazardous chemicals** in the lab is subject of a manual put together by NRC's Committee on Hazardous Substances in the Laboratory. **Page 25**

Preliminary Program

- **The society's spring national meeting** in Las Vegas will have more than 260 technical sessions; information on registration, housing, and special events, and coupon for advance registration are provided. **Page 28**

Surfactants—a mature market with potential

Growth in surfactants' use has been slow for long time, but there may be some surprises: enhanced oil recovery may be big market

Patricia L. Layman
C&EN, New York

It's big, it's mature, and it's marking time. That is one way to sum up the U.S. surfactant market as it works its way through the decade.

It is big, certainly: 7 billion lb in 1980, according to Colin A. Houston, president of the consulting firm C. A. Houston & Associates, Mamaroneck, N.Y. And it's expected to grow to 8.3 billion lb in 1991. That's a simple 2% year growth—the indication of a mature industry.

The general feeling among industry marketers seems to be that, with a few specialty exceptions, there is not a lot happening right now in the world of surfactants. For the time being, they say, there'll be more of the same—slow, steady growth in a business dominated by a single market (household cleaning and personal care products) and a larger but more fragmented set of industrial applications.

That's assuming everything goes along as normal, but the chances are that things won't. And with at least two potential wild cards in the deck, surfactant marketers are waiting.

The one most people are waiting for is the prospect of a market opening up for surfactants in enhanced oil recovery. This potential market offers the promise of consuming tremendous quantities of surfactants, even more than the household-personal care segment of the market by 1990. Or it may take much less, although still a significant amount. The end of this decade will give a clearer indication of what the demand will be, but for now, it all comes down to the degree of optimism of the forecaster.

Only about 30 to 40% of the oil in a reservoir can be recovered with

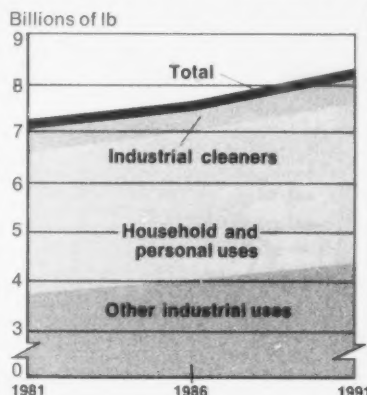
present conventional technology, even using water flooding. That leaves a powerfully attractive target still in the ground, and surfactants are high on the list of potential alternative methods for oil recovery. In 1979, consultant Houston estimates, only about \$105 million worth of chemicals, including services, were used in oil-field processing for tertiary, or enhanced, recovery.

But surfactant suppliers are hoping for big growth for the enhanced recovery technology, which involves variations on a theme of pumping surfactant solutions down into a well formation to scrub out oil from formation rock and basically push the oil, now mixed with water and surfactant, to a producing well.

That's the theory, and, indeed, it does work, initial tests indicate. But it is an uncontrollable process. One major oil company, for example, terms its tests a failure. "We know the oil moved," reports a marketing manager, "but we never could find where it moved to."

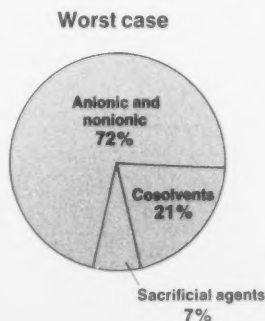
Nevertheless, surfactant marketers predict that the technology will become increasingly important, particularly in the form of micellar-polymer flooding. In this technique, water is pumped into a reservoir to

U.S. surfactant output will grow slowly next decade



flush out undesirable ions, using sacrificial agents such as lignosulfonates, nitrilotriacetic acid, or inorganic phosphates. Surfactants then are injected to scrub oil from the rock, polymer-thickened water is added to push oil and surfactants out of the rock, and a final injection of more water moves the whole mess to producing wells. Major surfactants presently used are petroleum sulfo-

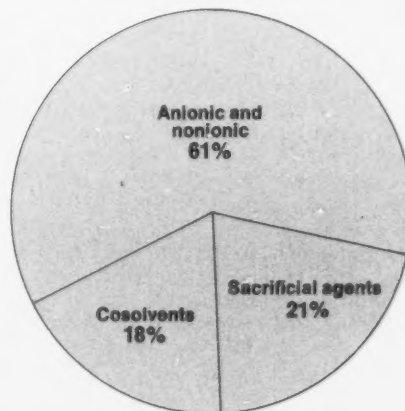
Enhanced-oil-recovery surfactants could top 3 billion lb by 1990



Total = 635 million lb

Source: Colin A. Houston & Associates

Best case



Total = 3.13 billion lb

Nonionics: Shell leads in higher-priced products

Nonionic surfactants, led by 12- to 18-carbon alcohol ethoxylates, got their big boost from another segment of the chemical industry—synthetic fibers. As more and more synthetics made their way into the typical laundry, detergent makers discovered that anionic surfactants, a whiz at the hot-water cleaning of cottons, are not as effective at the lower temperatures recommended for laundering synthetics. Nonionic sur-

factants are effective at lower temperatures, and also tend to be more effective on oily dirt—body oils, for example—and they started making their way into household detergent formulations.

Additionally, nonionics—by definition an ionically neutral compound consisting of an organic hydrophobe containing, usually, adducts of ethylene oxide—tend to be somewhat resist-

ant to hard-water ions. So when phosphate builders were banned from household detergents in some areas of the country, areas which ironically usually had hard-water supplies, and less-effective sequesterants were formulated into products instead, nonionics gave good performance. They won't interact with other components of a formulation, such as cationic fabric softeners. That way formulators can build more complex products that can offer a consumer or industrial customer better performance.

Processing of nonionic surfactants can present problems, because they don't spray-dry well. But they are easier to incorporate into liquid detergents than are anionic surfactants, so nonionics also got a boost by the rise in popularity of heavy-duty liquid detergents. From a market niche quietly occupied by Lever Brothers' Wisk, back in the 1950s, the market took off in 1970. Liquids then had about 4% of the household detergent market; now they hold almost 20%.

Most nonionic-surfactant capacity is merchant, as is that for raw materials. Procter & Gamble is one of the major captive producers of detergent alcohols, for example, but even that detergent maker hints that its present expansion also may aim at products for lubricant additives and chemical intermediates—which might or might not be captive.

C₁₂+ alcohols

	Capacity ^a
Shell Chemical	550
Ethyl Corp.	210
Conoco	135
Procter & Gamble	120
Sherex Chemical	20
TOTAL	1035
PRICE	68 to 72 cents/lb

Ethylene oxide

	Capacity ^a
Union Carbide	2170
Dow Chemical	710
Shell Chemical	700
Texaco	700
Celanese	250
TOTAL	4530
PRICE	32 cents/lb

Alcohol ethoxylate

	Capacity ^a
Shell Chemical	600
Union Carbide	150
DeSoto	190
Conoco	95
Texaco	85
TOTAL	1030
PRICE	56 to 57 cents/lb

Alkylphenol ethoxylate

	Capacity ^a
Rohm & Haas	80
Schenectady Chemicals	70
Borg-Warner	60
Monsanto	45
Texaco	35
TOTAL	290
PRICE	51 to 52 cents/lb

^a Millions of pounds per year. Source: SRI International

nates, but more specialized or tailored surfactants, including naphthalene sulfonates, and alcohol and alkylphenol ethoxylates are beginning to be used, adds Houston, who predicts a "base case" 1990 market of 635 million lb of surfactants for enhanced oil recovery—and an "optimistic case" of about 3.13 billion lb.

The other wild card—for the household detergent side of the business—is NTA, the trisodium salt of nitrilotriacetic acid. In the early 1970s, it seemed to be the major contender to replace sodium tripolyphosphate, then under attack as a contributor to waterway eutrophication. But environmental questions regarding carcinogenicity arose, and at the request of the U.S. Surgeon General, detergent makers voluntarily dropped use of NTA. However, after exhaustive tests—one supplier grumbled that NTA was "the most thoroughly tested consumer chemical" he knew—the Environmental Protection Agency in 1980 gave the

compound at least a lukewarm bill of health, declaring that, at least for the time being, it saw no reason to regulate NTA (C&EN, June 2, 1980, page 6).

With that encouragement, detergent makers turned their attention back to NTA, which not only is an efficient sequesterant of hard-water ions, but also is cost-competitive with phosphates. Procter & Gamble is testing several NTA-built versions of Tide and Oxydol—at present in nonphosphate areas.

And that, in turn, some marketers predict, may have a substantial impact on the surfactants used in heavy-duty powder and liquid household detergents. One possible negative impact is that, to overcome some of the performance deficiencies with nonphosphate formulations that sometimes showed up, manufacturers boosted the concentration of surfactant—to overwhelm the water-hardness ions, in effect. If NTA can be used, it might permit a decrease

in the concentration of surfactant in a formulation.

Or, its use might mean a shift in the surfactants used. SRI International, for example, predicts that use of NTA will allow manufacturers to turn to less-expensive surfactants that are highly sensitive to hard water. That, in particular, would mean alcohol sulfates, made and used by Procter & Gamble. SRI suggests that tallow-based alcohol sulfate suffered in performance in nonphosphate areas, which also happen frequently to have hard water supplies. Thus concentrations of alcohol sulfates were either reduced or eliminated in products sold in those areas. Alcohol sulfates already have been reintroduced to Procter & Gamble formulations built with zeolites, which had improved the sequestering action. If NTA, an even better builder, is used on a big scale, it will mean even more demand for alcohol sulfates, much beyond the 78 million lb expected to be used in

laundry powders in 1984. Consumption in 1980 was an estimated 68 million lb.

Procter & Gamble has used tallow alcohol sulfates since the late 1930s. But natural sources for surfactant raw materials have become a modern topic again, as suppliers eye stocks of coconut oil, palm oil, and tallow for their alcohols.

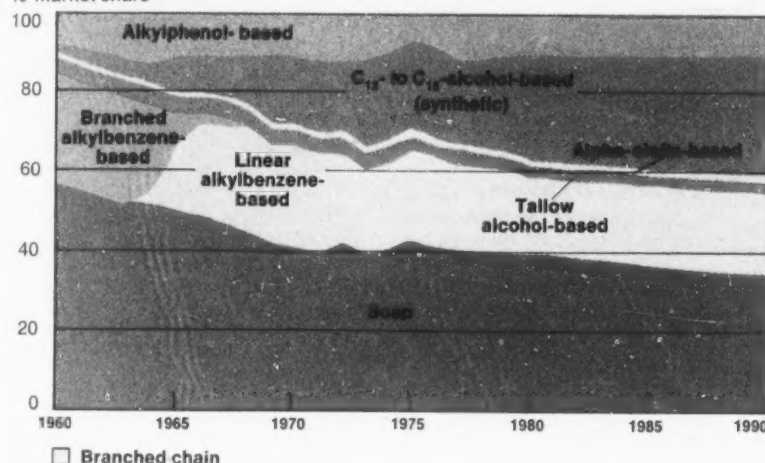
The industry basically splits into two factions, one headed by Shell Chemical and the other by Conoco. Shell, with its 550 million lb-per-year plant fed by petrochemicals for detergent alcohols (54% of U.S. detergent alcohol capacity), is sticking solidly with synthetics. Ethyl Corp., with 200 million lb per year of synthetic capacity, and Conoco, with 135 million lb, also are strong boosters of petrochemical-fed supplies.

But Conoco is hedging its bets. It is planning a 100 million to 120 million lb-per-year plant, to go on stream in 1984 or 1985, fed with natural oils. That plant is similar in size to the one Union Carbide and Henkel are planning for 1984, using Henkel technology. And Procter & Gamble, with 120 million lb of annual capacity using coconut oil, palm oil, and tallow, is expanding by another 65 million to 75 million lb per year. The remaining detergent alcohol producer, Sherex Chemical, is standing pat at 20 million lb.

More secure, though, is the promising outlook for alpha-olefin sulfonates (AOSs), with the fastest growth rate predicted for major surfactants. For years, AOSs were referred to as

Synthetic alcohols will make biggest gains in market

% market share



Source: Shell Chemical

"the next generation" of surfactants, but they went through some rough times before starting what looks like a solid growth phase. Introduced for detergents in 1969, AOSs were used that year at a level of about 14.3 million lb. Then Colgate-Palmolive formulated AOSs into its Palmolive dishwashing liquid, and by 1975, these compounds were being consumed at a rate of nearly 36 million lb a year. In 1976, however, Colgate reformulated, removing AOSs. The major reason was economics, but some environmental health questions also were raised, coming from tests

run in West Germany on AOSs' precursors. Use of AOSs dropped to 23 million lb in 1976, and within another year was down to 10 million lb—where it has stayed until recently.

From a solid niche in personal-care products, such as shampoos, AOSs have moved strongly into another shampoo-like formulation—the so-called liquid soaps. (The term is a misnomer because the formulations are synthetic detergents.) With a start from smaller manufacturers such as Jovan's Yardley unit and Minnetonka, liquid soaps have cap-

Specialty surfactants: where the action is

For producers of commodity or semi-commodity surfactants, the problem lies in meeting the shipping and specification demands of what is generally a few major customers. For producers of specialty surfactants, however, it's a true specialties business: many different customers, many different markets, small volumes tailored for specific end-uses, and prices on the high side.

Compared to an overall industry growth rate of 2 to 3% annually, specialty surfactants are featuring growth rates of 8 to 10% per year over the next few years. And producers figure that prices start at about 80 cents per lb, running up toward \$5.00 per lb, on a 100% active basis. Competition rests on good products, but even more important, on technical service. Companies have to develop the ability to listen to customers and tailor or mod-

ify surfactants to solve their problems in order to succeed. As with other specialty chemicals, service is all-important in marketing small-volume surfactants. Thus, while prices are high, the cost of selling is also high.

Instead of large or potentially large markets, marketers seek out niches. One marketer, for example, says his firm looked at supplying the enhanced oil recovery business, but then decided "You can't beat the big boys." Instead, specialty producers have turned to areas such as emulsifiers for cosmetics, flowing and wetting agents for agricultural chemicals, wetting agents for textile processing, and rubber-processing aids.

The cast of characters is different than that for commodity surfactants. Cationic surfactants are produced by companies such as Onyx, Lonza, Armark, and Sherex Chemical for ap-

plications ranging from hospital germicides to fabric and shampoo conditioners. Amphoteric surfactants, which tend to be exceptionally mild and nonirritating, are made by Mona Industries, Miranol Chemical, and American Cyanamid, in particular. And in the larger, specialty surfactants segment of the business, companies such as BASF Wyandotte, ICI Americas, GAF, Rohm & Haas, Emery Industries, and Diamond Shamrock frequently pop up, as well as a host of other, smaller producers.

As one market manager puts it, in the overall surfactants business, there are 700 different products, 200 different producers, and 450 different end-uses. That makes for a lot of company to compete for the large markets, and some awfully small niches for producers who want to single out a market for themselves.

Anionics: from workhorse to glamor entry

Although by some estimates, nonionic surfactants have nudged into first place in the household detergent and personal-care surfactant markets—the largest single grouping—anionics still have a larger share of the overall surfactants market.

Anionics, classically an organic hydrophobe on one end and an inorganic moiety such as a sulfate or sulfonate group at the other, continue to be the workhorses of the industry. Linear alkylbenzene sulfonate (LAS) is still used in most of the major brands of

household detergents, for example. Lignosulfonates, obtained mostly from spent pulping liquor of sulfite pulping operations, is a commodity surfactant, although "specialty" derivatives are used for such applications as concrete admixtures and drilling muds. And soap still accounts for some 35% of the market for major surfactants, used both in household products (primarily toilet soaps) and for industrial applications.

Most LAS is produced for captive consumption by Procter & Gamble, Colgate-Palmolive, Lever Brothers, and

Purex. Stepan Chemical and Onyx are among the major merchant sulfonaters, with a host of companies both sulfonating and sulfating a variety of commodity and specialty surfactants. Sulfonation capacity generally is inclusive, because a producer can process, with a few modifications, a number of raw materials. The sulfonation technology, developed by companies such as Chemithon and Lion, is reasonably easy to adopt, and this has encouraged small manufacturers to enter either captive or merchant production.

The sulfonation of alpha-olefin sulfonates (AOSs) is an exception. Although more companies (who already have sulfonation know-how) are entering the market, it still tends to be a specialized, and tricky, business. Some marketers feel that, in turn, has tended to limit the use of AOSs in formulated products; customers might be reluctant to commit themselves to purchasing AOS surfactants when they have produced other surfactants themselves and switching to buying rather than producing could mean idling already installed capacity.

AOSs are still a small segment of the business. The alpha-olefin capacity shown, for example, aims at markets far larger than the surfactant market, presently less than 20 million lb per year; it more likely aims instead at comonomers for linear low- and high-density polyethylenes, and at other specialty markets including synthetic lubricants.

Alpha olefin

	Capacity ^a
Ethyl Corp.	800
Shell Chemical	600
Gulf	200
Chevron U.S.A.	90
TOTAL	1690
PRICE	37 to 42 cents/lb

Linear alkylate

	Capacity ^a
Conoco	375
Monsanto	240
Union Carbide	160
Witco Chemical	45
TOTAL	820
PRICE	44 to 45 cents/lb

Sulfonated/sulfate surfactant

	Capacity ^a
MAJOR LAS PRODUCERS	
Procter & Gamble	570
Stepan Chemical	200
Colgate-Palmolive	190
Lever Brothers	170
Purex Industries	130
Onyx	100
TOTAL	1360
PRICE	54 cents/lb

	Capacity ^{a,b}
MAJOR AOS PRODUCERS	
Stepan Chemical	200
Onyx	100
Witco Chemical	60
Alcolac	39
Detergents Inc.	28
Henkel	25
TOTAL	452
PRICE	28 cents/lb

a Millions of pounds per year. b Includes LAS, other surfactants. Source: SRI International

tured 15 to 20% of the toilet soap market. That's enough to lure even the majors. Procter & Gamble, for example, is testing a liquid, dubbed Rejoice, in Texas. And although not all the liquid soaps contain AOSs, that still has been enough to give a boost to the products, to 12 million lb in 1980 and 13.6 million in 1981.

At present, use of AOSs is mostly limited to personal-care products. The environmental-health charges were laid to rest when the original test results were chalked up to what generally was agreed to be sloppy chemistry. But olefin makers point out there are some problems with interaction with sodium hypochlorite bleach—which has tended to keep the surfactant out of heavy-duty laundry products. That is expected to be resolved, however, with AOSs' moving into laundry powders. One supplier notes that the leading brand of detergent in Japan, marketed by

Lion Co., is based on AOSs. And Lion technology will be the basis of a new sulfonation unit being built by Detergents Inc., Santa Fe Springs, Calif., scheduled for completion April 1. It will have about 28 million lb-per-year capacity for processing not only AOSs but linear alkylbenzene sulfonate and alcohol sulfate.

For surfactant makers, another problem has arisen that may leave them with a sense of déjà vu: biodegradability, involving branched-chain alkylphenol (primarily nonylphenol) ethoxylates. By what one supplier calls "a gentlemen's agreement," use of the alkylphenol ethoxylates had been limited primarily to industrial applications, in which wastewater could be treated without discharge into the waterways. That harks back to the mid-1960s when the industry was pressured into switching from hard, branched-chain alkylbenzene sulfonates to the softer, more biode-

gradable, linear alkylbenzene sulfonates. The branched-chain material didn't readily biodegrade, and it began showing up as unesthetic foam in some water supplies.

The branched-chain alkylphenol ethoxylates have about the same biodegradability characteristics as the hard alkylbenzene sulfonates—that is to say, not much. But they are also quite a bit less expensive than either linear alkylbenzene sulfonates or alcohol ethoxylates, and that has been appealing to some of the smaller, economically hard-pressed detergent makers. They have been turning to alkylphenol ethoxylate, incorporating it into their formulations. The result? Alcohol suppliers have seen at least a tiny segment of their market eroding and, concerned that larger detergent makers also may switch to alkylphenol ethoxylates, have raised the issue again. □

NOTE

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Cover 1, p. 3, 33-34, 36,

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